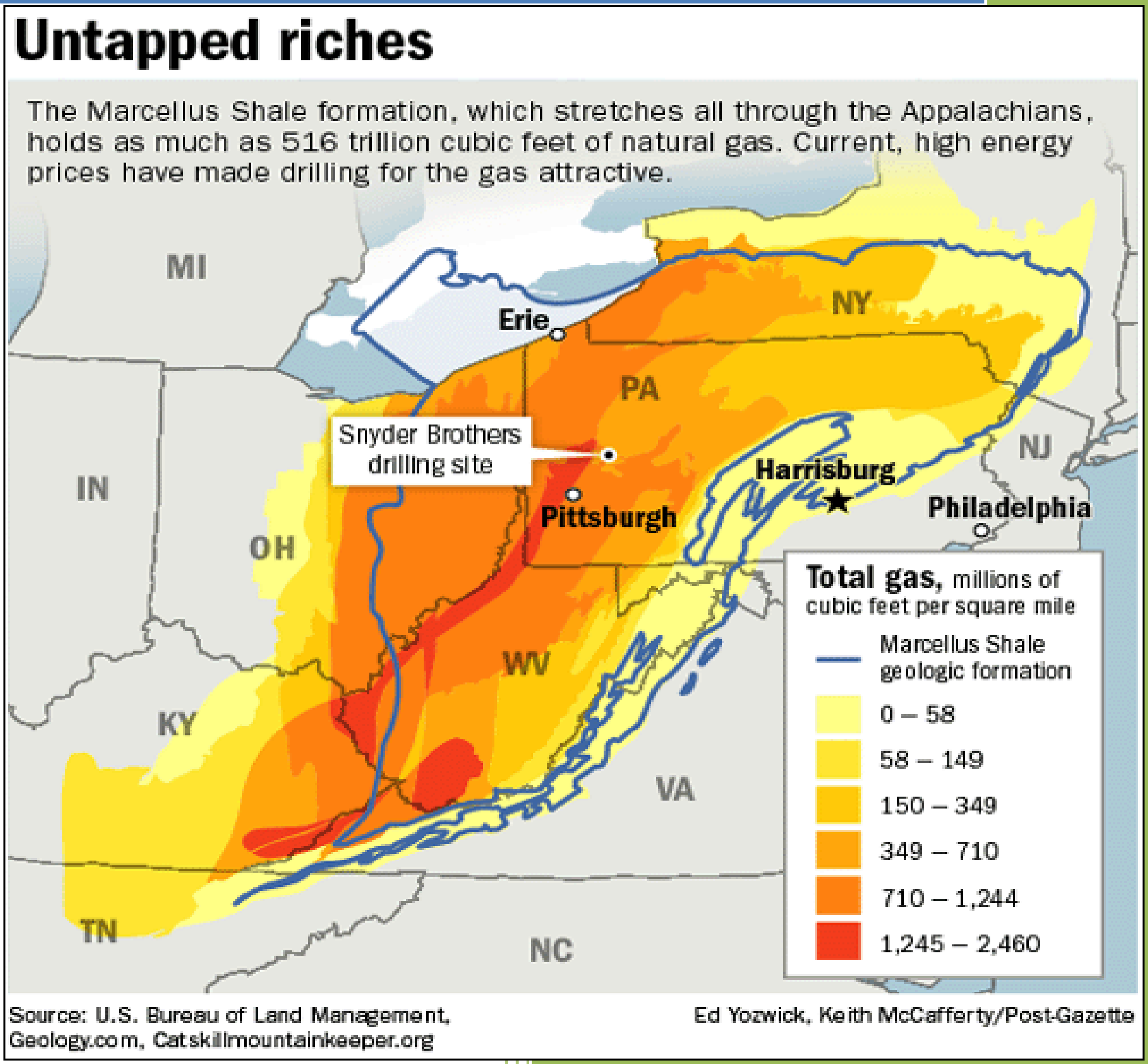
Marcellus Shale

Brine Water Pilot Study



Thomas A Angelo

City of Warren, Ohio

Water Pollution Control

5/4/2010

TABLE OF CONTENTS

OVERVIEW

In May of 2009, The City of Warren and Patriot Water Treatment LLC began discussions with the Ohio Environmental Protection Agency (OEPA) to initiate the treatment of brine water from the Marcellus Shale. A series of letters and meetings culminated to a letter issued to Warren by OEPA to perform an eight (8) week pilot study to "clearly identify the amount of brine that Warren can receive without causing WWTP or water quality issues."

Charged with this task, Warren first had a whole effluent toxicity (WET) test accomplished on September 4, 2009 to determine the ceiling of brine water acceptance. This demonstrated that the facility could accept up to 664,000 gallons of brine water at 50,000 mg/l TDS before toxic conditions caused a water flea kill. This was based on an 8 MGD flow. Knowing that typical flow rates are approximately 13.38 MGD allowed for a protective buffer of 5.38 MGD dilution ratio.

An organizational meeting was held January 8, 2010 to review current information and to set guidelines for the pilot study. The guidelines were set as follows:

- Patriot Water Systems would supply ten 20,000 gallon frac tanks.
- The tanks would be connected together to create one 100,000 gallon mixing system.
- Brine water would be re-circulated in the combined tanks to create a homogeneous mix.
- The initial mix will be tested for the parameters as defined by OEPA.
- The City will sample influent, effluent, upstream and downstream prior to the discharge of brine water to develop a baseline concentration of TDS.
- The City would conduct a live, 8 week, phased in trial to monitor and record effects on treatment processes, accumulation loading and receiving stream TDS.
- The maximum amount of TDS in the brine water will not exceed 50,000 mg/l.
- Brine water will be phased in as follows (all flows will be over an 8 hour period):
    - Week 1 – 5 days at 20,000 gallons
    - Week 2 – 5 days at 40,000 gallons
    - Week 3 – 5 days at 60,000 gallons
    - Week 4 – 5 days at 80,000 gallons
    - Week 5 – 5 days at 100,000 gallons
    - Week 6 – 5 days at 100,000 gallons
    - Week 7 – 5 days at 100,000 gallons
    - Week 8 – 5 days at 100,000 gallons
- Testing will be accomplished as defined in Addenda 3 (revised 3/1/10).

The pilot study was initiated on Tuesday, February 9, 2010. This required a deviation from the schedule because the first week did not start on a Monday. As a result, week 1 only had 4 days of discharge. The pilot was postponed mid way through week 2 because source water wasn't available due to extreme weather conditions making the remote well site locations inaccessible to truck traffic. The pilot study resumed on March 1, 2010 at 40,000 gallons per day and followed the documented schedule throughout the remainder of the study.

BASELINE SAMPLING

Initial baseline testing was accomplished on the river and plant flow to determine TDS levels prior to start-up of the pilot study. The baseline levels are as follows:

Baseline Levels	TDS	Chloride
Raw	584	143
Final	599	157
Up	336	70
Down	332	60
Liquid Sludge		296

Initial radioactivity sampling:

Collect date 2/17/10

Parameter	Results	Units
Gamma Scan	All other nuclides <LLD	pCi/L
K-40	2.6E+02 +/- 2.6E+01	pCi/L

K-40 is the radioactive isotope in Potassium. It is naturally occurring and common. The average human being carries approximately 140g of potassium. We ingest and excrete approximately 2.5g per day. Potassium has two other stable isotopes, K-39 and K-41. The most abundant is K-39 at 93.26% of the total. This is followed by K-41 at 6.73% and finally K-40 at 0.0188%. K-40 has a very long half-life, 1,260,000,000 years. Very little beta ray and gamma ray energy is released as it decays.

Potassium Content and Potassium-40 Activity in Some Selected Foods				
Food	Portion	Potassium [mg]	K-40 [µg]	Activity [Bq]
Hot Dog	1 plain @ 98 g	143	16.7	4.5
Double Hamburger	1 loaded @ 226 g	570	66.7	18.1
Chicken, roasted	¼ @ 195 g (light & dark)	447	52.3	14.2
French Fries (veg. oil)	10 strips @ 50 g	306	35.8	9.7
Broccoli (raw)	3 spears @ 93 g	302	35.3	9.6
Brewed Coffee (black)	250 mL @ 250 g	135	15.8	4.3
Banana	1 medium @ 150 g	454	53.1	14.4
Orange juice, chilled	250 mL @ 263 g	500	58.5	15.9
2% Milk	250 mL @ 258 g	398	46.6	12.6
Skim Milk	250 mL @ 259 g	429	50.2	13.6
Figs, dried, uncooked	10 @ 137 g	1331	155.7	42.2
Potato, baked, skin on	1 @ 202 g	844	98.7	26.8
Bran Flakes, Post™	175 mL @ 37 g	177	20.6	5.6
Maple syrup	15 mL @ 20 g	41	4.8	1.3
Whole Wheat Bread	1 slice @ 28 g	71	8.3	2.3
White Bread	1 slice @ 25 g	30	4.0	1.0
Sunflower Seeds, dried	75 mL @ 41 g	345	40.4	10.9
Peanut Butter	30 mL @ 32 g	234	27.4	7.4
Egg	1 large @ 33 g	47	5.0	1.5

Ram Chandrasekar, Ph. D., Manager of Lab Operations for the Bureau of Public Health Laboratories, Ohio Department of Health, provided this explanation on why Thorium tests were not conducted:

Subject: Thorium versus Gross Alpha
ODH Lab methods for radiological testing includes gross alpha screen which includes alpha emitted by Thorium nuclides. Hence if the gross alpha value is below the threshold value, there is no need to perform the Thorium estimation. When the initial gross alpha value is high, separate Thorium determination is required to identify the level.

PILOT STUDY

The pilot study commenced as scheduled with no other interruptions except for the one noted above. Sampling was accomplished as scheduled. OEPA was on site March 17, and March 31, 2010 and conducted sampling. At the time of this writing, the results of these samples have not been received.

The treatment operations did not have any adverse effects as a result of the introduction of brine water. The only operational issue that occurred was a result of Patriot discharging at a higher rate in order to meet gallons requirement before an assumed cut off time of 3:30pm. This produced a shock load that was identified in the sampling protocol but did not cause any disruptions to the biological flock or treatability of the wastewater, however some toxicology issues were noted on the April 2nd tests concerning chronic C. Dubia.

TDS OVERVIEW

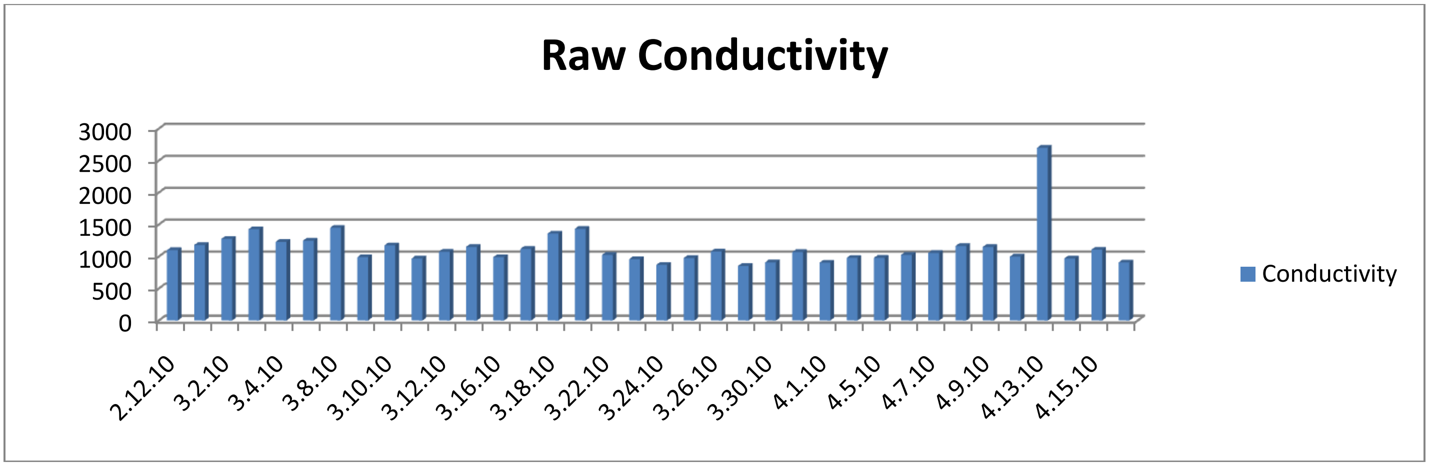
Sludge
Three (3) sludge samples were tested for Chlorides during the pilot study. The results of these samples are:

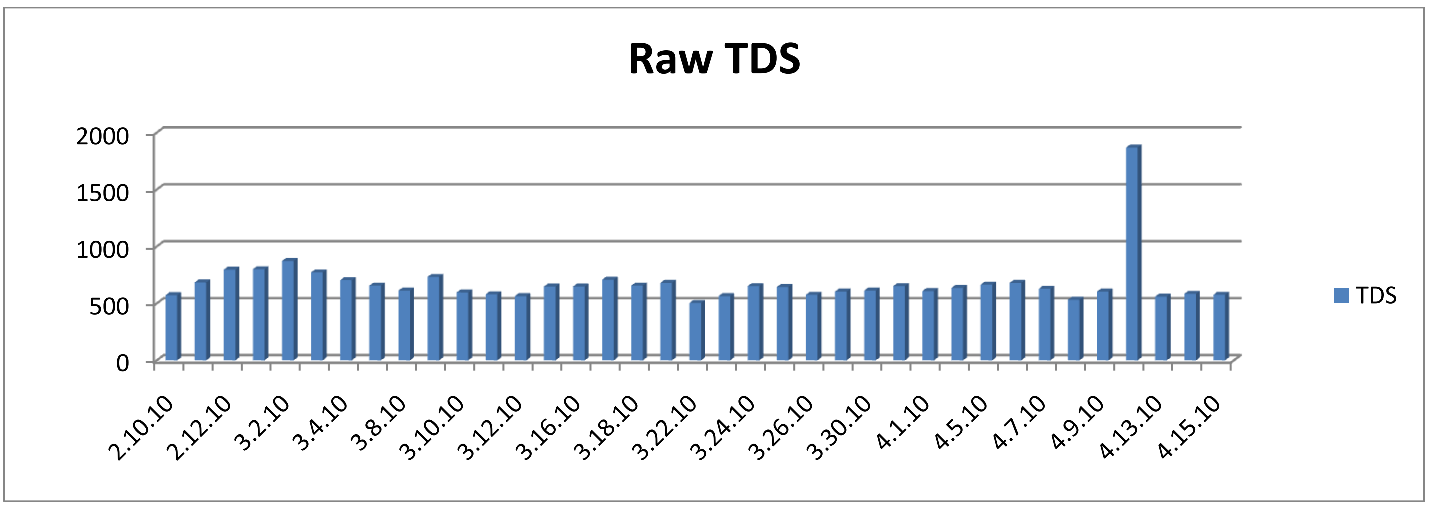
Sample Date	Chloride mg/Kg
2/17/2010	250
4/05/2010	184
4/16/2010	456

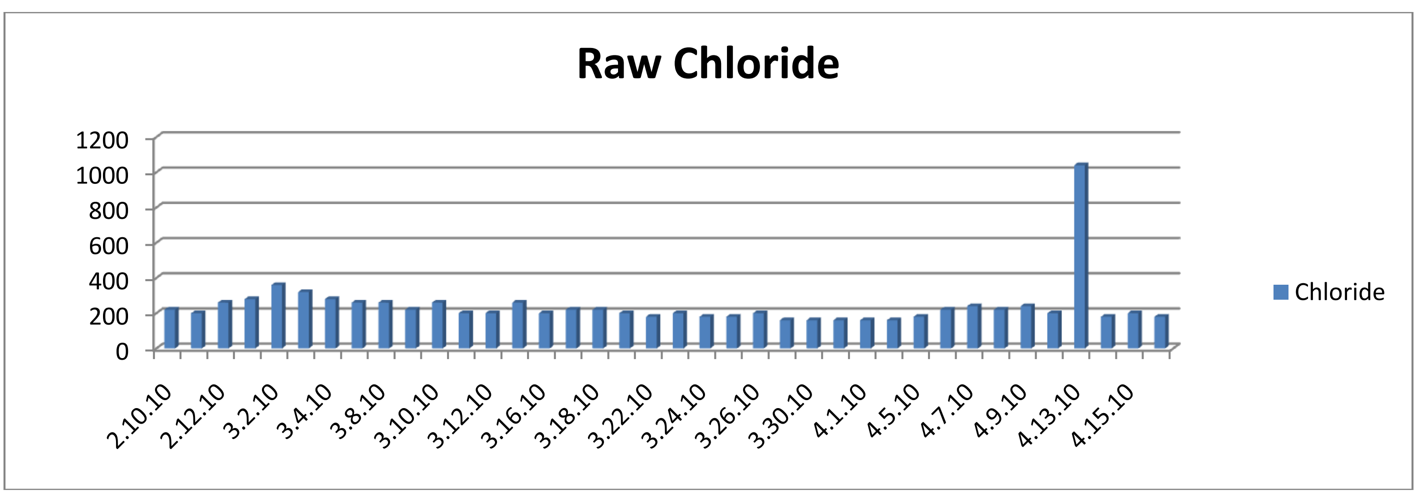
The increase in Chlorides in the sludge potentially can be a result of TDS becoming colloquial solids and settling. However, one data point does not provide sufficient evidence to make a clear determination. Therefore, additional observations will be necessary in order to see if this is actually occurring. If this is a fact, than a percentage of the brine water is actually being treated. Additional observations will allow for a percentage of treatment to be determined if this continues as a trend.

Raw Influent

The average raw TDS did not increase significantly over the 8 week pilot study. Raw TDS average increased to 679 mg/l which is approximately 16% over the baseline of 584 mg/l. Raw chlorides averaged 239 mg/l which is approximately 67% more than the baseline of 143 mg/l. These increases are most likely due to seasonal fluctuations within the collection system as a result of user operations or seasonal runoff from spring rains. (Raw does not have any Patriot Influence or plant return flows)

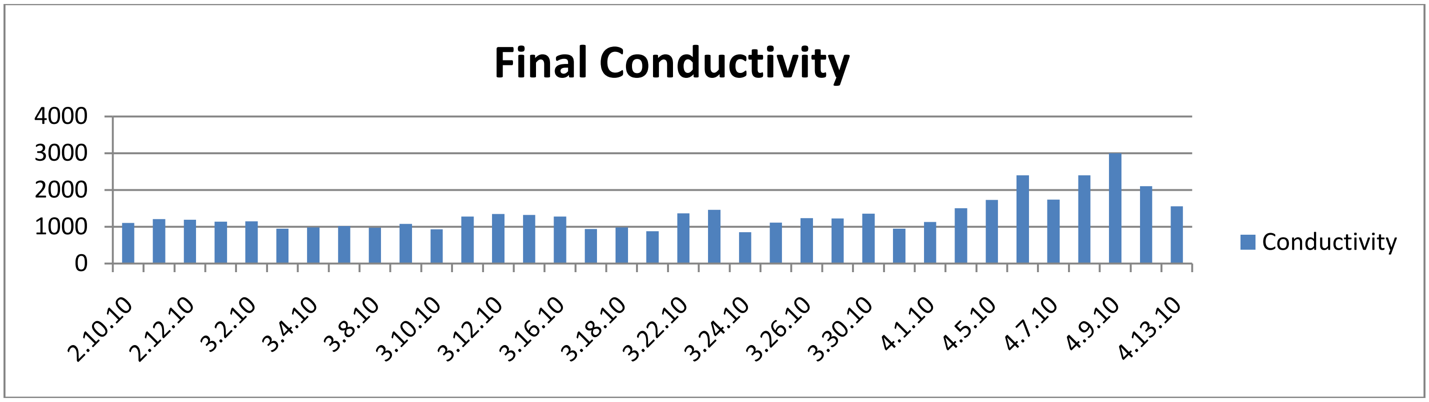


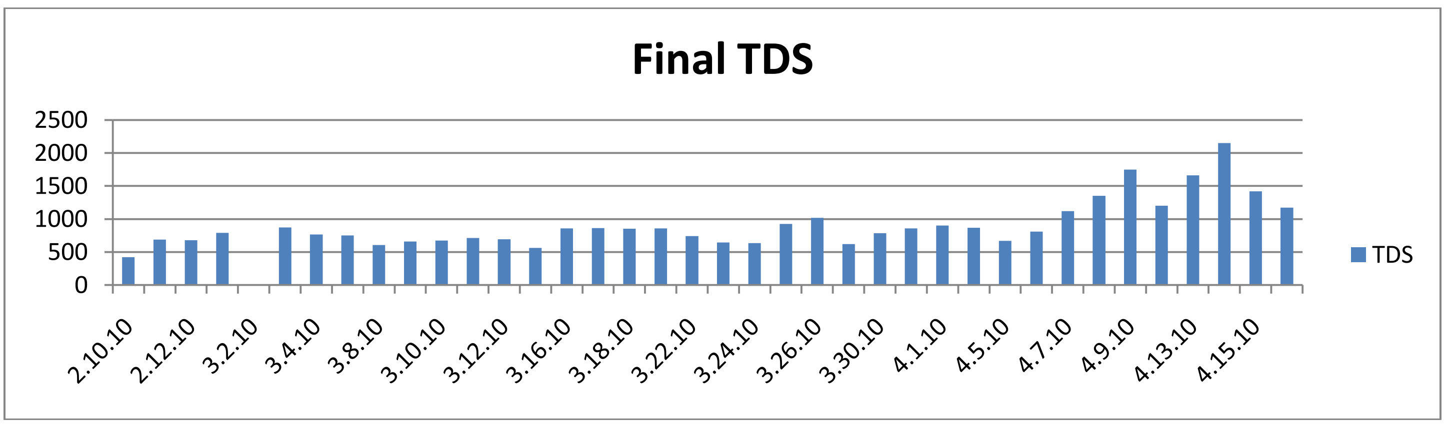


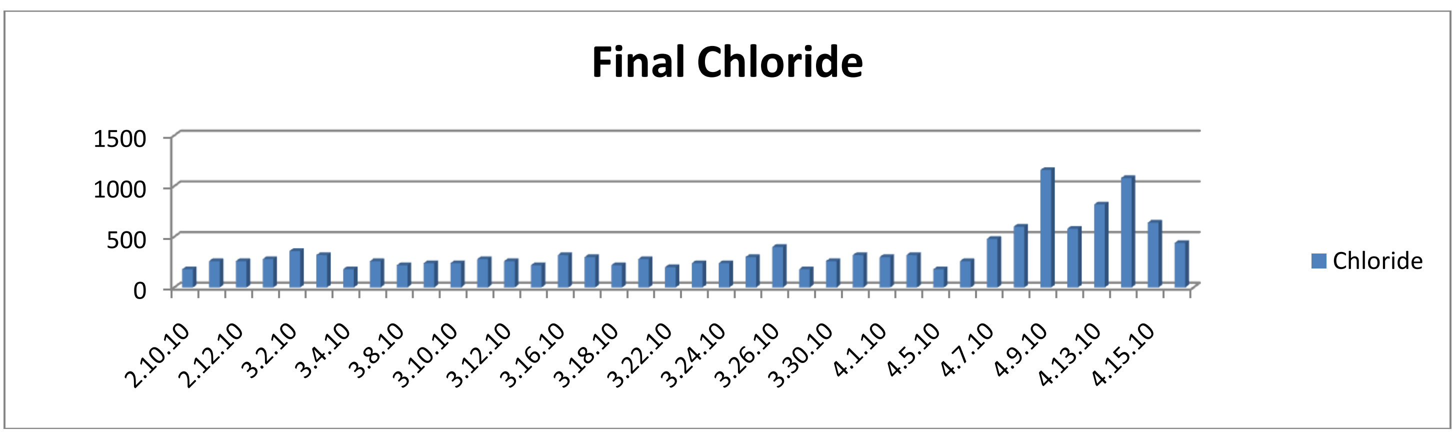


Final Effluent

The average final effluent TDS increased by 47.8% above the baseline to 885 mg/l and the average final effluent Chlorides increased by 122% over the baseline to 348 mg/l. This was expected as most of the TDS would pass through the system. However, since raw chlorides increased at a greater percentage than raw TDS, it cannot be ruled out that seasonal fluctuations within the collection system, as a result of user operations and spring rains, may be causing these increases. The higher increases in chlorides in both the raw and final could have resulted from runoff water from the roads entering the collection system during early spring rains. These rains would have carried additional salt that had acuminated from winter de-icing procedures and was washed off the roads with the spring rains. Infiltration and Inflow into the collection system would have allowed this additional source of salts to add to the overall total. While the timeline, as demonstrated by the graphs below, suggest that this hypothesis may be accurate, it also coincides with the increase to 100,000 gallons per day discharge of brine. Additional observations, during this critical period of time, will help to establish if the hypothesis is accurate.

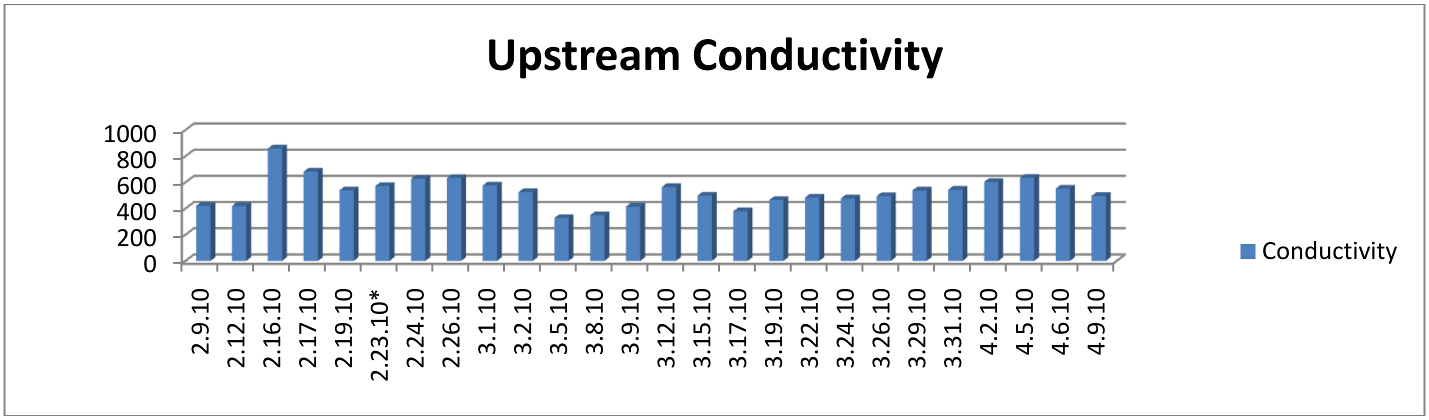


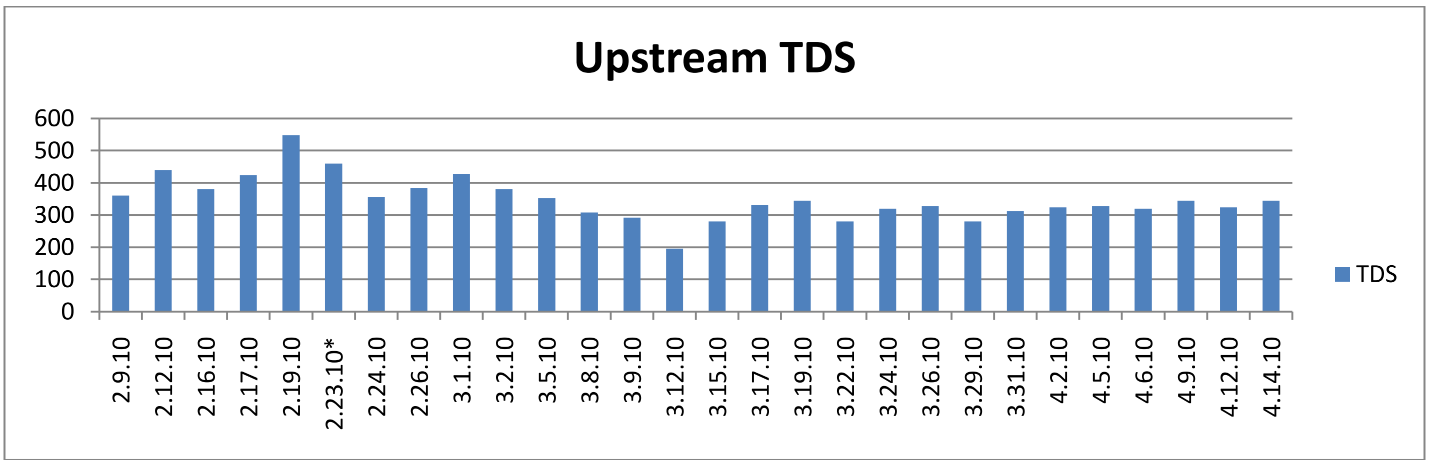


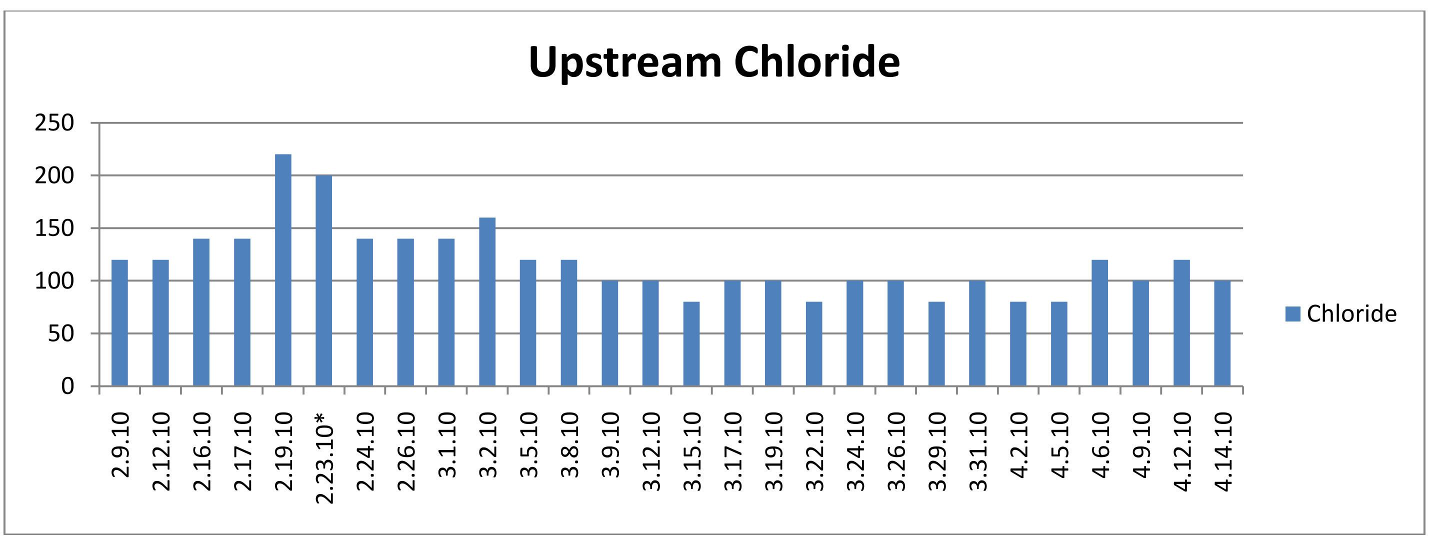


River - Upstream

The average Upstream River TDS of 348 mg/l remained close to the baseline value of 336 mg/l. This represents an increase of 3.6%. However, the average chlorides, at 123 mg/l, were 76% higher than the baseline of 70 mg/l. This is most likely due to seasonal de-icing practices where salts applied to roadways were washed into the river from storm outlets.

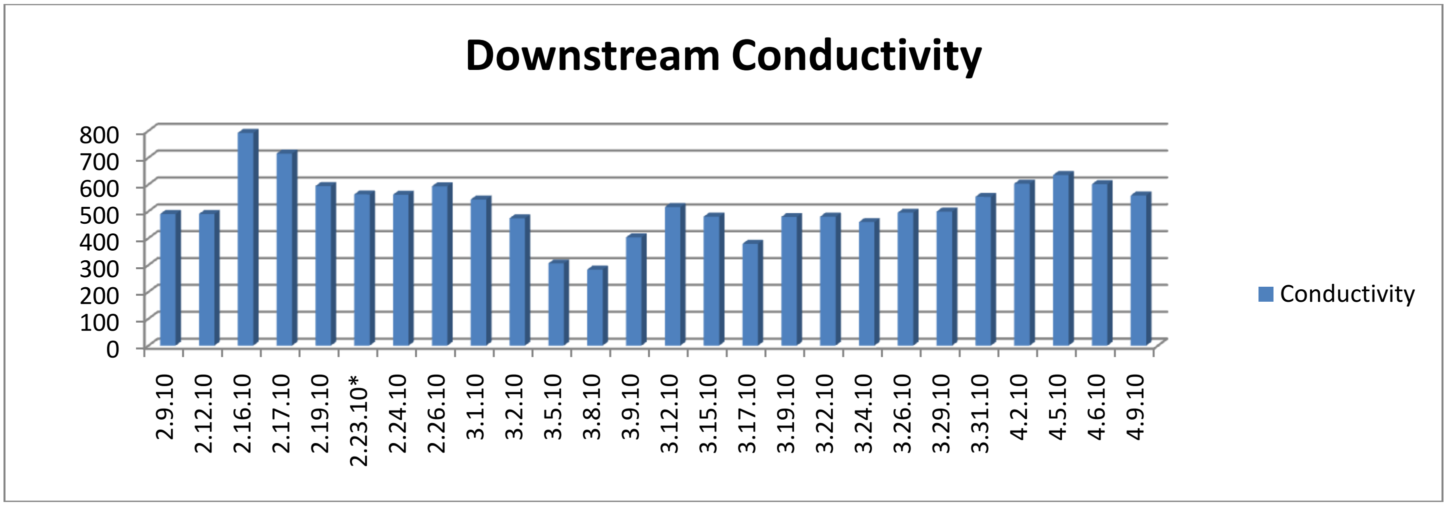


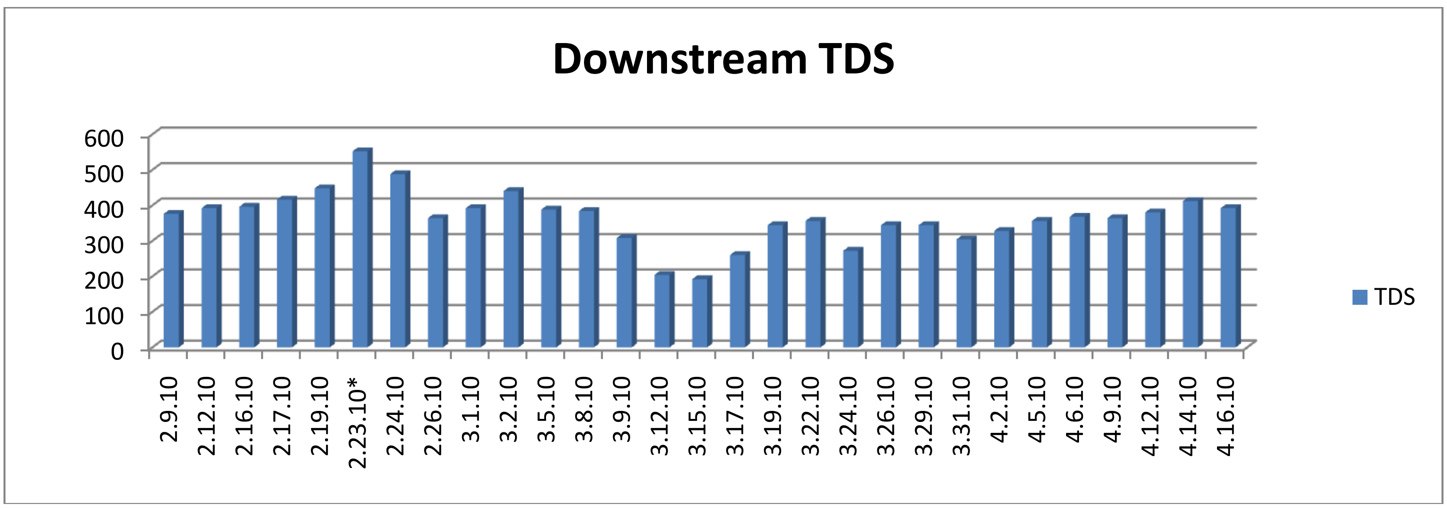


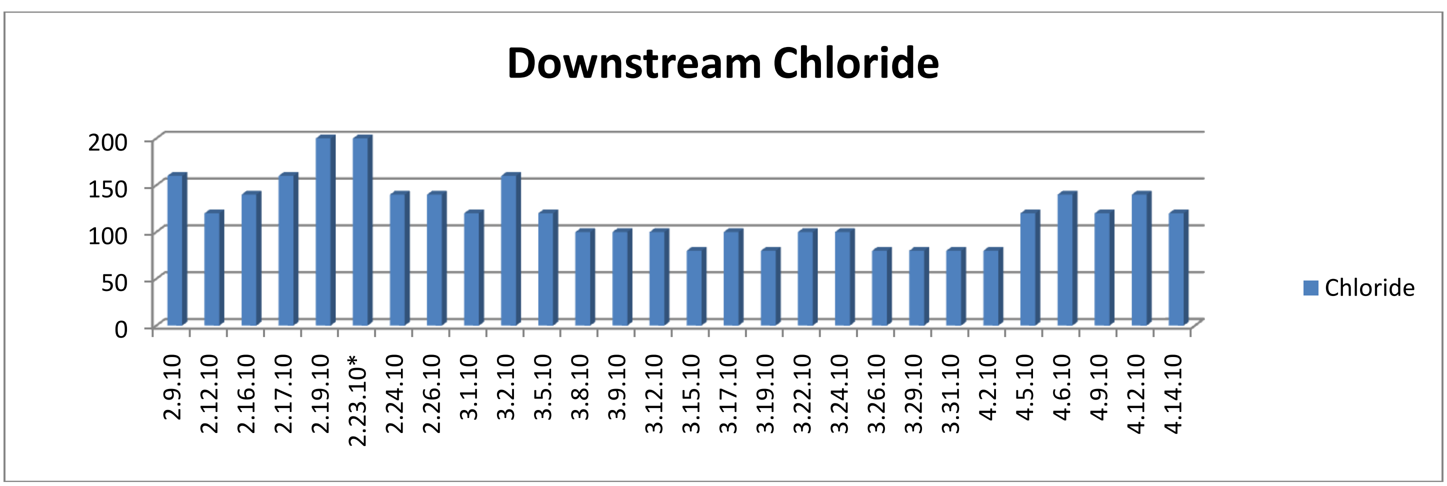


River – Downstream

The average Downstream River TDS of 364 mg/l remained close to the baseline value of 332 mg/l. This represents an increase of 9.7%. However, the average chlorides, at 121 mg/l, were 81% higher than the baseline of 67 mg/l. The majority of this increase is most likely due to seasonal de-icing practices where salts applied to roadways were washed into the river from storm outlets. This is evidenced by the deviation as already noted in the Upstream Chlorides. The additional increase of 5% from Upstream to Downstream would include chlorides from non-point sources along the river way and the introduction of chlorides from the brine water study.







Toxicology

Date	Ceriodaphnia dubia		Pimephales promelas	
	TUa	TUc	TUa	TUc
February 20, 2010	AA	AA	-	-
March 6, 2010	AA	AA	-	-
March 13, 2010	AA	AA	-	-
March 20, 2010	AA	AA	-	-
March 27, 2010	AA	AA	-	-
April 3, 2010	AA	1.8	-	-
April 10, 2010	AA	AA	-	-
April 17, 2010	AA	AA	AA	AA

AA = below detectable limit

Patriot Water Treatment in conjunction with Warren WWTP performed 8 weeks of chronic toxicity testing to determine whether the release of brine from Patriot Water Treatment would impact the water quality of Warren WWTP effluent discharged from Outfall 001. Although it is not required in Warren's NPDES permit, receiving water samples were taken and tested alongside the effluent samples to give insight into the overall water quality of the Mahoning River (receiving stream) and determine any impacts the effluent may have after it is discharged. Due to the fact that increased salt concentrations impact *Ceriodaphnia dubia* more readily than the *Pimephales promelas*, the water fleas were the primary species used in this study, however, during the last week of testing the minnows were subjected to the brine water also to investigate any potential impacts.

The data from 8 weeks of toxicity tests is summarized in the table above. As indicated by the results no increased toxicity was observed from the brine water provided by Patriot Water Treatment with the exception of one testing event, April 3, 2010. This test was unique as compared to the others due to some confusion by Patriot on dispersal rates of the brine. This week, due to outside influences not controlled by Patriot Water Treatment, the brine was released in large slugs over a short period of time instead of the previous slow release over 8 hours as was done in previous weeks and the last 2 weeks of sample collection. Due to the large slugs of water released there was more potential to pick up a large amount of brine during the sampling process and this is the probable cause of toxicity observed to the water fleas. The slug loads occurred due to disruptions in discharge flow to accommodate Septic Sewerage Sludge contractors. The same line was used by the contractors as Patriot. Patriot was supposed to discharge the 100,000 gallons over an 8 hour period but was also instructed to stop discharge by 3:30pm. These two conflicting directives caused the slug loads. After Warren was made aware of the conflict, Patriot was instructed to maintain the 8 hour requirement even if it meant that discharge would continue past 3:30pm. This operational correction resolved the problems.

There was some effect seen intermittently in the upstream and farfield receiving water samples. The largest impacts were observed in the upstream water which is outside of the influence of the effluent. These effects are not indicative of toxicity as a result of Warren's effluent or Patriot's brine water. The two testing events that indicated toxicity in the upstream receiving water showed that the toxicity was reduced or no longer present in the farfield water samples.

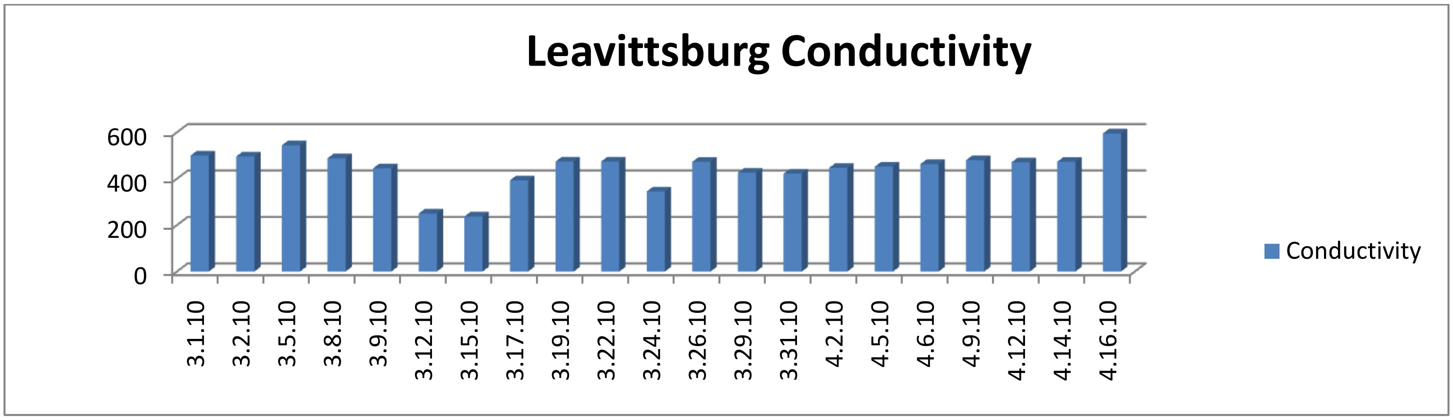
Overall the results of this study have indicated that if Patriot Water Treatment discharges a consistent amount of brine water over an extended period of time then there will be no adverse changes in the water quality of Warren WWTP or in the Mahoning River downstream of outfall 001.

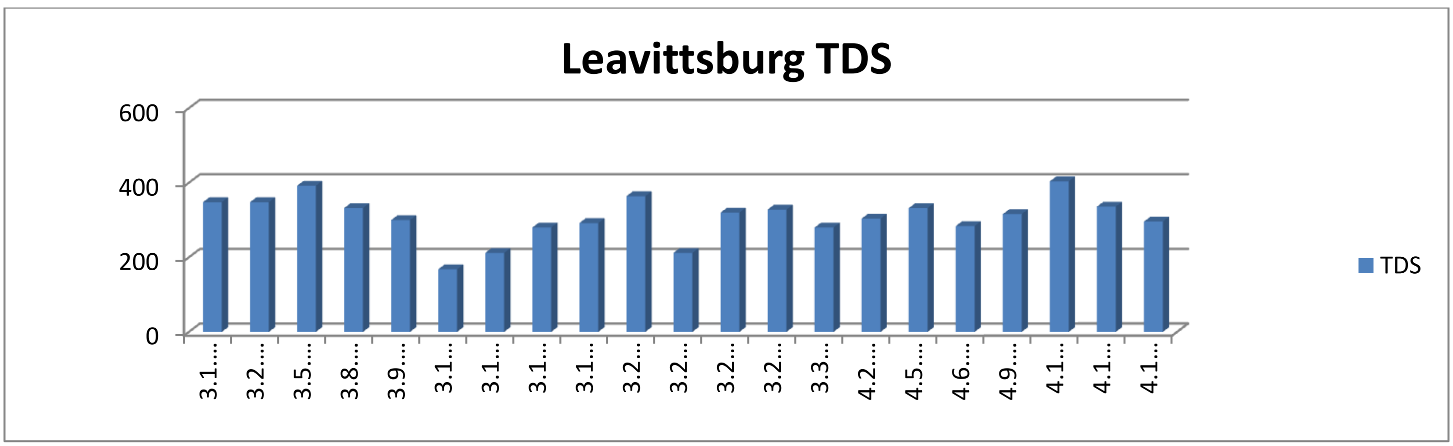
Additional Sampling

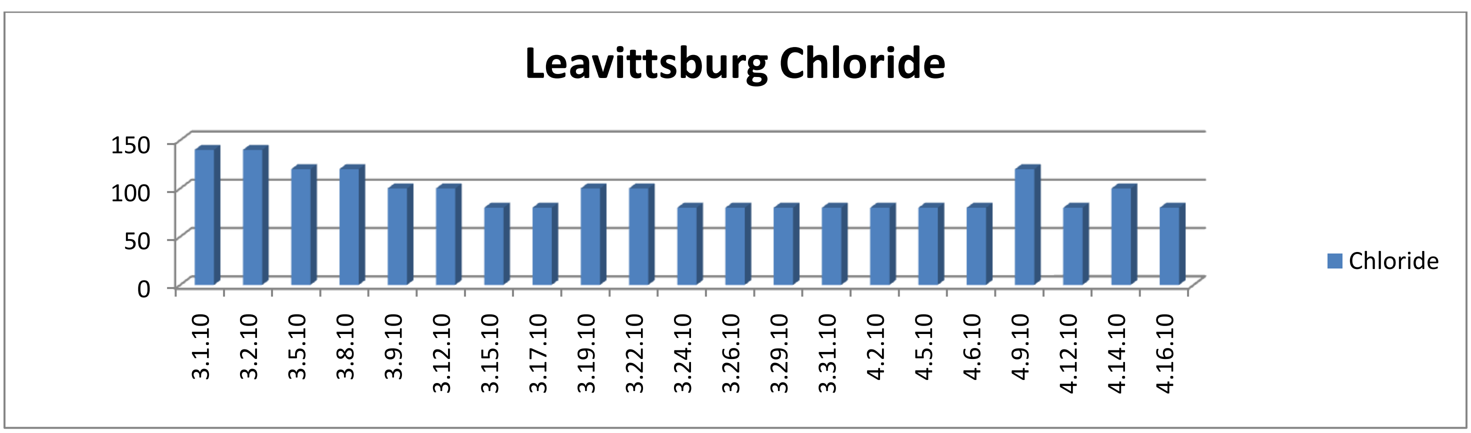
To better understand the impact of TDS on the receiving stream, Warren expanded sampling points to better model what was occurring throughout the Pilot Study. Two additional sampling points were added for the river. These sampling points were the North Leavitt Road bridge in Leavittsburg, Ohio and Belmont Road bridge in Niles, Ohio. These two points were sampled every Monday, Wednesday and Friday or as close to these days as possible. Sampling began on March 1, 2010. Averages for the additional sampling points were:

Leavittsburg	TDS – 307 mg/l	Chlorides – 96 mg/l
Niles	TDS – 347 mg/l	Chlorides – 123 mg/l

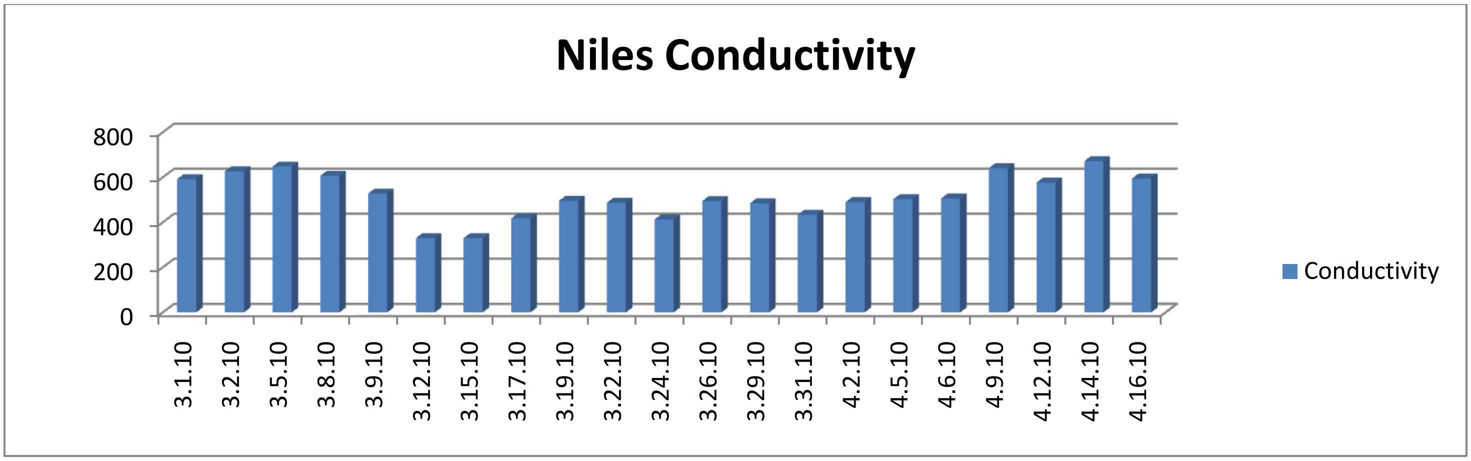
Leavittsburg Sampling

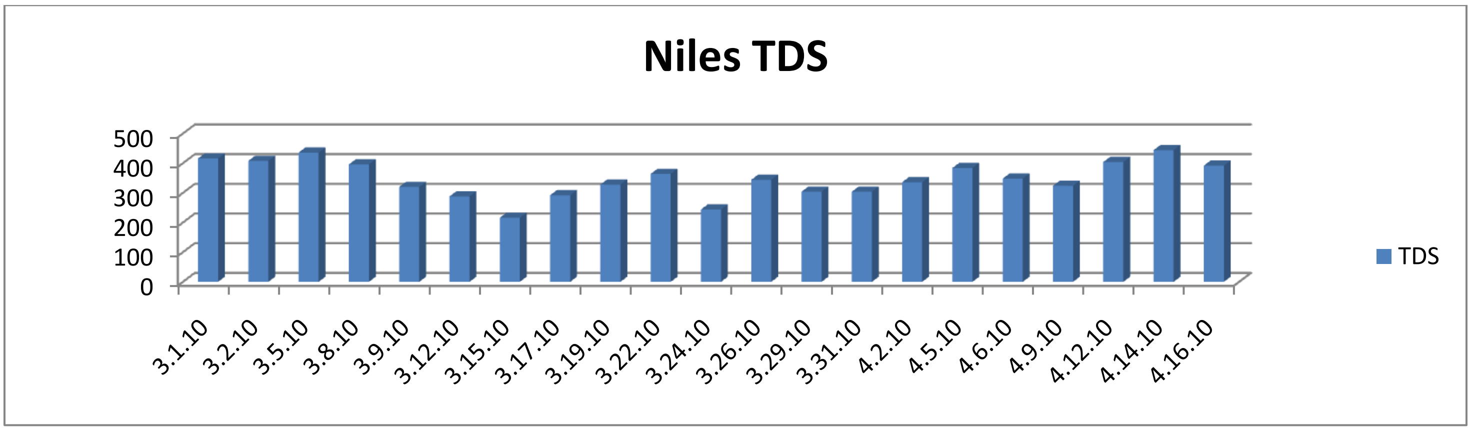


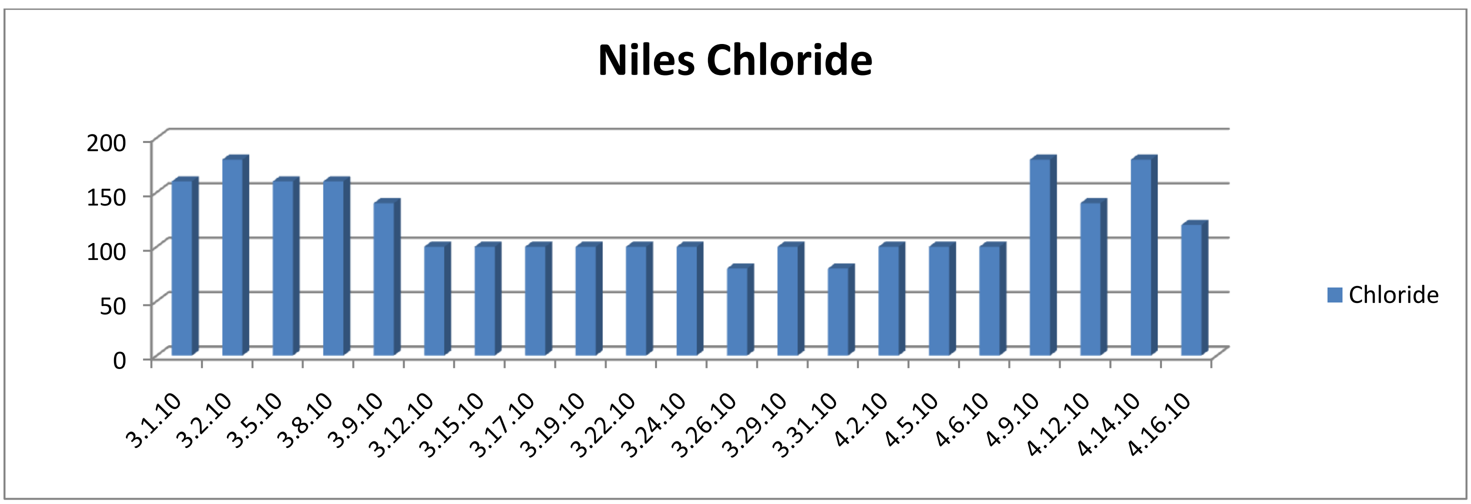




Niles Sampling







Youngstown Sampling

Youngstown's WWTP was asked to provide values that will establish baseline information for future evaluations in watershed modeling. Denise Seman, Lab Manager for Youngstown WWTP, provided the following information from samples obtained on April 6, 2010:

Raw TDS –	851 mg/l	Final TDS –	881 mg/l
Upstream TDS -	431 mg/l	Downstream TDS -	543 mg/l

Conclusion

The 8 week Pilot Study demonstrated that a controlled discharge of brine water into Warren's WWTP did not have adverse water quality impacts to the treatment facility or receiving stream. The Study supports the initial toxicology test that indicated that Warren would be able to accept up to 664,000 gallons per day of brine water at a maximum limit of 50,000 mg/l TDS at 8 MGD daily plant flows. The 8 MGD is set as the low flow limit that can occur in mid-summer at 3:00am.

Warren should be able to begin accepting brine water at the initial rate of 100,000 gallons per day and increase amounts at a controlled rate, while sampling, to determine final ceiling concentration.

Next Steps

The existing Pilot Study equipment should be used as a transitional system while final review, PTI and NPDES modifications are completed. A flow rate of no more than 200,000 gallons per day, over a 16 hour discharge period, will be allowed for the transitional system. Administrative Orders will be assigned to establish operational procedures, local and categorical limits and testing frequencies. Transference to the permanent location will allow for metals precipitation to occur. Sampling protocols should require that all parameters as defined within the Pilot Study will be accomplished on a monthly basis, except for radioactivity, for the first 6 months of operational discharge. Sampling frequencies for all parameters as defined within the Pilot Study, after 6 months will be quarterly for an additional year. Sampling frequencies after that time will be established based on data accumulated and will be set at that time.

Additional WWTP's that wish to provide treatment services will have to first perform a baseline toxicology test, using their effluent flows, to determine ceiling limits. Flow rates will then be allowed at a phased in approach as established by the Pilot Study proportional to their minimum plant flows. Testing of final effluent and farfield toxicology, TDS and Chlorides will be accomplished at least bi-weekly as a control.

Warren looks forward to assisting Ohio in developing this new and potentially viable industry. As such, I am offering my assistance in developing a watershed model to determine total TMDL loading. I wish to thank OEPA for the opportunity to conduct the Pilot Study and look forward to working with OEPA and USEPA on establishing procedures that will impact users in Ohio and hopefully set the model for our neighboring states.

Respectfully Submitted

Thomas A. Angelo

Addenda 1

Sampling Protocol

Samples were collected at each of the described locations following proper sample handling, collecting and preserving techniques outlined in the USEPA manual Methods for Chemical Analysis of Water and Wastes.

Brine Samples: Patriot employees collected Brine samples from storage tanks (frequently referred to as Frac tanks). The tanks had a pumping system that was intended to keep the tanks from settling and provide representative samples. All of the samples collected from the brine tanks were grab samples. The brine or frac tanks were located in front of the WWTP Screen Building and discharged into the plant approximately 6 feet after the raw wastewater sampling location.

Raw Samples: City of Warren Wastewater Operators collected samples of the raw waste stream. Raw composite samples came from the permanently located sampling device that sits outside of the Screen building. The sampler generally collects a 24-hour sample beginning and ending at approximately 7 am daily. During the study we also collected an 8-hour sample at approximately 3 pm to check the total dissolved solids in the time frame that Patriot was discharging to the influent. Grab samples were obtained from the same location at a removable grate just in front of the raw composite sampler. The Brine discharge was located about 6 feet downstream of the raw sampling point.

Final Samples: City of Warren wastewater Operators collected samples of the final effluent. Final composite samples are collected from a permanent sampling device located in a lower level room of the facility near the return activated sludge pumps (RAS). Final composite samples are also collected as a 24-hour sample that runs approximately from 7 am to 7am daily. During the study we also collected an 8-hour sample to represent the 24-hour detention time of the plant. Grab samples of final effluent were collected at the post aeration tanks just before going over the weir to the underground pipe that leads to the outfall.

Upstream River Samples: City of Warren Sewer crew staff collected samples of the upstream Mahoning River. All samples collected from the upstream river were grab samples. The samples were collected at the bridge just inside of the Severstal Steel property.

Downstream River Samples: City of Warren Sewer crew staff collected samples of the downstream Mahoning River. All samples collected representing the downstream river were grab samples collected at the West Park Street Bridge.

Upstream 2 Leavittsburg River samples (further upstream 2): City of Warren Sewer crew staff collected samples of the Leavittsburg further upstream Mahoning River. All samples collected representing the upstream 2 were grab samples collected at the North Leavitt Street Bridge.

Downstream 2 Niles River samples (further downstream 2): City of Warren Sewer crew staff collected samples of the Niles area further downstream 2 Mahoning River. All samples collected representing the downstream 2 were grab samples collected at the bridge on Belmont Street in Niles.

During the 8-week study the Wastewater treatment plant experienced no observable negative impacts. Microscopic examination of the activated sludge verified that there were plenty of active free-swimming ciliates and stalked ciliates along with other single celled organisms. Our normal testing parameters were all within acceptable ranges. As a matter of fact, during the study the average for final effluent Ammonia-Nitrogen was about 0.4mg/L, which demonstrates that the nitrifiers were alive and active in the activated sludge.

When looking at the Conductivity and Total Dissolved Solids (TDS) there is a potential for the TDS results to be skewed higher than they actually are due to formation of a water-trapping crust. In Standard Methods, the TDS method recommends drying at $180^{o}C$ but allows for drying at other temperatures. It is thought that drying at $180^{o}C$ will result in more complete conversion of bicarbonate to carbonate. Since we did not have a drying oven that could be dedicated to the TDS test, we used our Total Suspended Solids (TSS) drying oven, which operates at $105^{o}C$. When comparing the measured TDS and calculated TDS it is appropriate for the measured TDS to be up to 20% greater than the calculated TDS (Standard Methods 1030 E).

Addenda 2

WPC River Sampling Locations
Upstream Mahoning River

Directions to Upstream Sampling Location:

1. Turn right out of WPC plant driveway on to Austintown Warren Road (Main Street) heading northbound 0.9 miles to Dover SW.
2. Turn right onto Sever stal Steel Bridge (private entrance)

WPC River Sampling Locations
Downstream Mahoning River

Directions to Downstream Sampling Location:

1. Turn left out of WPC Plant driveway heading southbound 1.4 miles to West Park Ave.
2. Turn left onto West Park Street eastbound 0.9 miles to the West Park Street Bridge.

WPC River Sampling Locations
Upstream 2 Leavittsburg Mahoning River

Directions to Upstream 2 Sampling Location:

1. Turn right out of WPC plant onto Austintown-Warren Road northbound 2.2 miles
2. Turn left onto South Ave. SW (route 422) westbound 3.2 miles to North Leavitt Road.
3. Turn right onto North Leavitt Bridge.

WPC River Sampling Locations
Downstream 2 Niles Mahoning River

Directions to Downstream 2 Niles Sampling Location:

1. Turn left out of WPC plant onto Austintown-Warren Road southbound 1.4 miles to West Park Ave.
2. Turn left onto West Park Ave. eastbound 2.1 miles to Main Street (route 46)
3. Turn right onto Main Street (route 46) southbound 0.8 miles to McKees Lane.
4. Turn left onto McKees Lane eastbound 0.7 miles to Belmont.
5. Turn left on Belmont northbound 0.3 miles to bridge.

Addenda 3
Testing Schedule

Warren WWTP Test Study: Oil and Gas Well Production Wastewater
Required Analyses

B - Beginning of eight week test period **T - End of eight week test**
D - Daily **W - End of each Monday-Friday 5 day test period**
A - As needed, or non-routine (e.g., after rain event)

Parameter	001	Influent after return streams	801	901	Sludge[1]	
Acute toxicity, *ceriodaphia dubia*	W[3]		W[3]	W[3]		
Acute toxicity, *pimephales promelas*	T[3]		T[3]	T[3]		
Chronic toxicity, *ceriodaphia dubia*	W		W	W		
Chronic toxicity, *pimephales promelas*	T		T	T		
Specific conductivity	D, A[5]	D, A[5]	W, A	W, A		
Total dissolved solids	W, A[4, 5]	W, A[4, 5]	W, A[4]	W, A[4]		
Chlorides	W, A[4]	W, A[4]	W, A[4]	W, A[4]	B, T	
Fluorides	T, A	T, A	T, A	T, A	B, T	
Sulfates	T, A	T, A	T, A	T, A		
total alkalinity	T, A	T, A	T, A	T, A		
total suspended solids	T, A	T, A	T, A	T, A		
total phosphorus	T, A	T, A	T, A	T, A		
pH	W	W	W	W		
HEM oil and grease	T	T	T	T		
SGT-HEM oil and grease	T	T	T	T		
Metals[2]	T				B, T[6]	
Barium, Strontium[8]	**W**	**W**				
Low level mercury	T					
Hexavalent chromium	T					
Volatile organic compounds	T					
Base neutral organic compounds	T					
Acid organic compounds, including pesticides and total phenols	T					
MBAS	T					
$CBOD_5$	T					
COD	T					
total organic carbon (TOC)	T					
Total nitrogen	T					
Ammonia-nitrogen	T					
Nitrate/nitrite nitrogen	T					
Total alpha radiation in pCi/l	W, T B				B, T	pCi/g
Total beta radiation in pCi/l	W, T B				B, T	"
Total uranium in pCi/l	T, W, B				~~A~~ B T	"
Total radium in pCi/l (or Ra 226 + Ra 228),	T, W, B				~~A~~ B T	"
Total thorium in pCi/l	T, W, B				~~A~~ B T	"

Warren Test Parameter Table_r1
February 10, 2010

* ADD to STUDY Requirements

Notes:

1. Sludge after dewatering, before processing
2. Metals (for sludge see note 5): aluminum, antimony, silver, ~~barium~~, beryllium, boron, cadmium, chromium, copper, iron, nickel, lead, selenium, ~~strontium~~, zinc
3. Calculated endpoint
4. Conduct analyses on WET test samples
5. To develop a brine specific TDS/specific conductivity ratio
6. Metals regulated by 40 CFR 503
7. Required if there is a significant increase in total alpha or total beta radiation
8. During 100,000 gpd weeks